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Research Article

Synthesis of bulk lanthanum polyphosphate and other rare earth phosphates through hydrothermal hot-pressing

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Abstract: Bulk samples of lanthanum polyphosphate were synthesized through a hydrothermal hot-pressing (HHP) process. In this process, pressing temperature, pressure and volume of water were varied in order to improve the density and strength of the resulting materials. The strength of the bulk samples was estimated through drilling and ultrasonic treatments. In order to improve the strength of the materials, the use of microwave irradiation was examined. Lanthanum polyphosphate formed porous bulk samples with a filling factor of approximately 70%, which was calculated from real and theoretical densities. With respect to machinable strength, a drilled hole greater than 7.0 mm in diameter was obtained on some bulk samples, and the diameter of the samples was 14 mm. The HHP process is a useful method for obtaining bulk samples of lanthanum polyphosphate. Bulk lanthanum polyphosphate containing water crumbled easily to a powder form upon ultrasonication. However, these bulk samples retained their shape upon ultrasonication, despite containing water, after exposure to microwave irradiation, and also experienced minimal weight loss. Furthermore, to study the effect of microwave heating, bulk lanthanum orthophosphate, yttrium orthophosphate and polyphosphate were also examined.

Keywords: lanthanum polyphosphate; hydrothermal hot-pressing (HHP) process; machinable strength; vibration strength; microwave heating

1 Introduction

Phosphates have been widely utilized as ceramic materials, catalysts, adsorbents, fluorescent materials, dielectric substances, metal surface treatments, fertilizers, detergents, food additives, fuel cells and pigments. Of all the known phosphate materials, rare earth phosphates are particularly important, owing to their high melting points and low solubilities in acidic and basic solutions [1].

For their various applications, phosphates can be in the form of powders, bulk samples, or thin layers. As phosphates decompose to oxides at high temperatures through the loss of P_2O_5, it is difficult to obtain bulk samples of phosphates through standard sintering techniques. As a novel synthetic process, the use of hydrothermal hot-pressing (HHP) method has been investigated [2–7]. In this method, a mixture containing the powder starting material and a small amount of water is sintered at relatively low temperatures, which typically produces porous phosphate materials. The advantages of this method are

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low sintering temperatures and porous bulk products that it typically produces. However, although many porous phosphate bulk samples have been synthesized through HHP, these bulk samples are not physically strong enough for use in many applications. Therefore, it is necessary to improve the physical strength of bulk samples; this physical strength is related to the filling factor. The filling factor is calculated by the real and theoretical densities, and the bulk samples with a high filling factor typically possess high physical strength. The strength against the mechanical processing is also an important factor in the formation of phosphate bulk samples. Bulk samples with a high density are usually hard; however, they may also be fragile. The porous structure can be deformed by the impact of mechanical treatment. Another important factor to consider is how the sample pellet can contain water easily during the HHP process, as microwave heating is expected to sinter the sample pellet in a short duration of time.

In this study, lanthanum polyphosphate was synthesized by heating a mixture of lanthanum oxide and phosphoric acid, and subsequently subjecting it to the HHP process. The lanthanum polyphosphate bulk samples were assessed by examining their density, filling factor, machinable strength and vibration strength. Bulk samples heated with microwave irradiation were also examined. Furthermore, in order to study the machinability and vibration strength of bulk rare earth phosphates, lanthanum orthophosphate, yttrium orthophosphate and polyphosphate were used.

2 Experiment

Lanthanum oxide, La_2O_3, was mixed with phosphoric acid in the molar ratio of La:P = 1:3. This ratio was determined from the chemical composition of lanthanum polyphosphate, $La(PO_3)_3$. The mixture was then heated at 700 ℃ for 1 h. The resulting product was characterized by X-ray diffraction (XRD) analyses. The XRD patterns were recorded on an X-ray diffractometer (MiniFlex; Rigaku Corp.) using monochromatic Cu Kα radiation (30 kV, 15 mA, 3 (°)/min).

The mixtures of the sample powders (1 g) and water (0–0.4 ml) were placed in a mold and mechanically pressed with a uniaxial pressure of 5–30 MPa for 1 h, using the HHP process. As the mold had a slight excess of space, water could be volatilized during the sintering process. The filling factor was calculated using the density of the obtained lanthanum polyphosphate bulk samples and the ideal density of the crystallized lanthanum polyphosphate.

The machinable strength was estimated from the diameter of a hole that was drilled into the 14 mm-diameter pellet. The vibration strength was estimated by the following method. Bulk samples were first placed in a 100 ml beaker with 100 ml of water, and then ultrasonicated for 60 s. The bulk samples were then collected and dried, and the weight loss was calculated. In order to improve the strength prior to ultrasonic treatment, the bulk samples were heated by microwave irradiation (2450 MHz, EMO-706; IRIS OHYAMA INC.). Because phosphate bulk materials contained a small amount of water, the effects of sintering by microwave irradiation for a short duration were expected. As a comparison to the microwave-heated bulk samples, bulk phosphates were also heated with an electrical furnace under ambient conditions.

Furthermore, other rare earth phosphates were also used to study the effects of microwave heating. Lanthanum orthophosphate, $LaPO_4$, was synthesized by heating a mixture of La_2O_3 and phosphoric acid in the ratio of La:P = 1:1 at 700 ℃ for 1 h. Yttrium ortho- and polyphosphates were obtained by heating the mixtures of yttrium oxide and phosphoric acid in Y:P = 1:1 and Y:P = 1:3 at 700 ℃ for 1 h, respectively. Also, these phosphates were then subjected to the HHP process. The obtained bulk rare earth phosphates were examined with the same method as the bulk lanthanum polyphosphate.

3 Results and discussion

3.1 Chemical composition of lanthanum polyphosphates

Figure 1 shows the XRD pattern of the sample prepared with the ratio of La:P = 1:3; this sample exhibits the peaks of lanthanum polyphosphate, $La(PO_3)_3$. Other compounds are not detected in the XRD pattern of the sample. In this work, the XRD patterns of the samples do not change after the HHP process, microwave heating, or calcination in an electric furnace. It is important to note that the samples display no change in the XRD patterns after sintering.

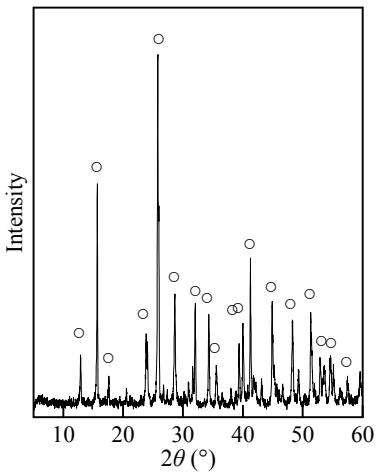


Fig. 1 XRD pattern of the sample prepared with La:P = 1:3; ○: $La(PO_3)_3$.

3.2 Density of bulk lanthanum polyphosphates

The density of the bulk samples is an important property owing to its correlation with its physical strength. Figures 2–4 show the densities and filling factors of lanthanum phosphate bulk samples. Temperature does not have a strong influence on the density of the lanthanum phosphate bulk samples (Fig. 2). The filling factor is approximately 70%, which is calculated from the ideal density of lanthanum polyphosphate. This percentage is lower than that of the phosphate bulk samples synthesized by the HHP process in the previous experiments [8–10]. The low filling factor can potentially absorb the physical stress. The phosphate bulk samples synthesized with 0.1 ml of water exhibit a higher density than those synthesized without any water (Figs. 2 and 3). The increase in the volume of added water indicates a weak ability to improve the density of bulk samples synthesized through the HHP process (Fig. 3). As the pressure used in the HHP process increases, the bulk density typically improves (Fig. 4).

3.3 Machinable strength of bulk lanthanum polyphosphates

In addition to the physical strength of bulk samples, the change of the bulk shape is an important factor in its use as a material [11]. Inorganic materials are generally resilient to physical stress, but may be prone to cracking because of mechanical treatment. Therefore, the strength against mechanical treatment is

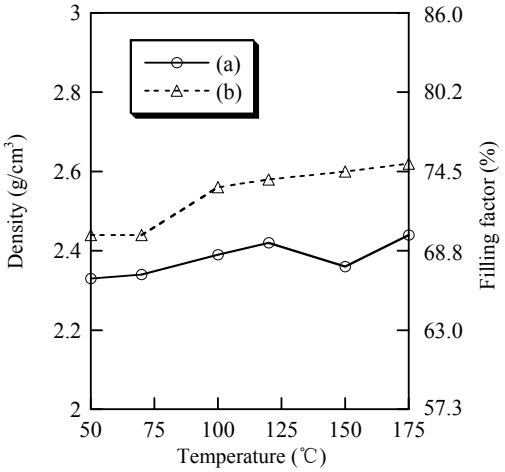


Fig. 2 Temperature effects on the density and filling factor of the bulk lanthanum polyphosphates with water volume of (a) 0 ml and (b) 0.1 ml (20 MPa).

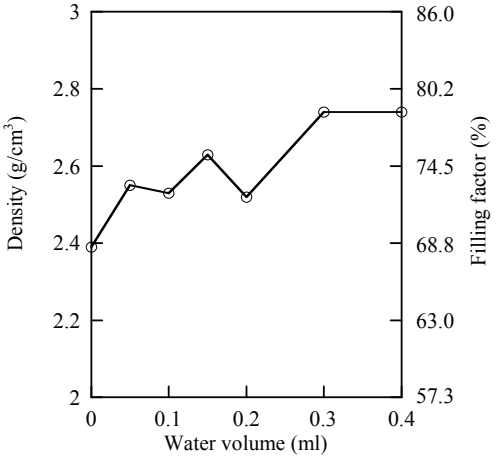


Fig. 3 Water volume in relation to the density and filling factor of the bulk lanthanum polyphosphates (100 ℃, 20 MPa).

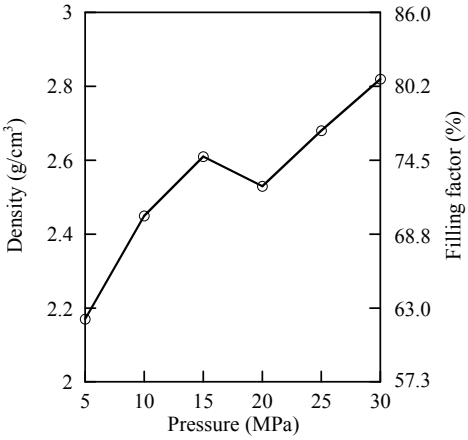
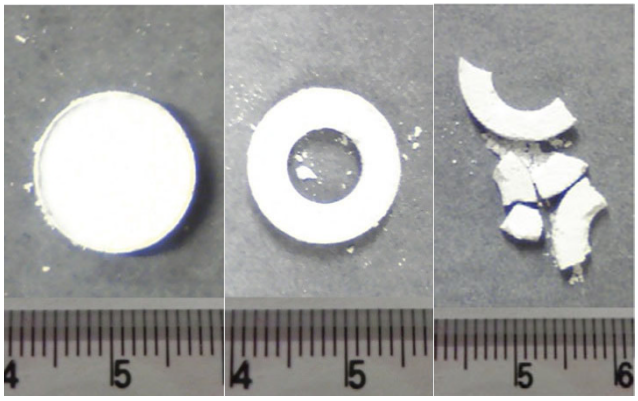


Fig. 4 Pressure effects on the density and filling factor of the bulk lanthanum polyphosphates (100 ℃, water volume = 0.1 ml).

studied by using a drilling process. Figure 5 shows the photographs of bulk samples before and after drilling treatment. The bulk samples have diameter of 14 mm. The diameter of the drill begins at 4.0 mm, and increases at a rate of 0.5 mm for each additional test. The maximum diameter obtained without the cracking is recorded for the phosphate bulk samples.

Table 1 shows the maximum diameter of drilling for the lanthanum polyphosphate bulk samples prior to cracking. The mark "x" corresponds to no record, or that the bulk samples were cracked by the 4.0 mm drill. The bulk sample synthesized at 100 ℃ with 0.4 ml of water is the only sample with no record. In the previous studies [12], cracking occurred in many bulk samples synthesized from lanthanum orthophosphate. Lanthanum polyphosphate bulk samples are typically more resistant to drilling than lanthanum orthophosphate bulk samples. Since the samples prepared with the ratio of La:P = 1:3 have a higher machinable strength than the samples prepared with the ratio of La:P = 1:1, the phosphorus-rich composition is related to the stickiness against physical stress. Many conditions produce a drilled hole with a diameter larger than 6.0 mm. A drilled hole greater than 7.0 mm is obtained on some bulk samples with a diameter of 14 mm for the entire sample. The pressing temperature, pressure and volume of water do not have a clear influence on the strength of the bulk materials against the drilling.



(a) (b) (c)

Fig. 5 Photographs of the lanthanum polyphosphate bulk samples: (a) without mechanical treatment; (b) after drilling a hole with a diameter of 7.0 mm; (c) after drilling a hole with a diameter of 7.5 mm.

Table 1 Maximum diameters of the drilled holes in the bulk lanthanum polyphosphates without cracking: (I) temperature dependence, 20 MPa; (II) pressure dependence, 100 ℃; (III) volume of water dependence, 100 ℃ (Unit: mm)

(I)	Temperature (℃)				
Water volume (ml)	50	70	100	120	150
0	5.5	4.0	4.5	6.0	5.0
0.1	5.5	6.0	4.5	4.0	4.5
(II)	Pressure (MPa)				
Water volume (ml)	5	10	15	20	25
0.1	4.0	6.0	4.0	4.5	7.0
(III)	Water volume (ml)				
Pressure (MPa)	0	0.1	0.2	0.3	0.4
20	4.5	4.5	6.0	4.0	x

3.4 Vibration strength of bulk lanthanum polyphosphates

In previous work, the bulk samples synthesized by HHP were weak to ultrasonication in water [12]. Since the bulk samples can easily contain water, microwave heating for a short amount of time is expected to improve the strength of bulk phosphates in water. Therefore, some bulk samples were put in water after microwave irradiation, treated with ultrasonication, and then collected. The weight loss of bulk samples is shown in Table 2. A small weight loss corresponds to high vibration strength in the bulk phosphates. The bulk samples that were not heated in the microwave crumbled to powders in water before ultrasonic treatment (Table 2(a)). Alternatively, bulk samples heated in a microwave display little weight loss after ultrasonic treatment (Table 2(b), Table 2(c) and Table 2(d)). The microwave irradiation is effective in maintaining the bulk shape in water. After ultrasonic treatment for 180 s, the weight loss of the bulk sample becomes large (Table 2(e)). The weight loss is about 20% for the bulk sample synthesized at 150 ℃ (Table 2(f)). Since the samples lose water as a result of the high pressing temperature, the microwave heating effect is minimal. Bulk samples synthesized at 10 MPa without water crumbled to powders in water after ultrasonic treatment for 60 s (Table 2(g) and Table 2(h)). The 10 MPa pressure is too low, and the bulk sample obtained without water is not greatly affected by microwave heating.

Table 2 Weight losses of bulk lanthanum polyphosphates

	Pressure (MPa)	Water (ml)	Temperature (℃)	Microwave (s)	Ultrasound (s)	Weight loss (%)
(a)	20	0.1	100	0	60	100
(b)	20	0.1	100	30	60	7.24
(c)	20	0.1	100	60	60	4.38
(d)	20	0.1	100	180	60	6.34
(e)	20	0.1	100	30	180	59.28
(f)	20	0.1	150	30	60	22.50
(g)	10	0.1	100	30	60	100
(h)	20	0	100	30	60	100

3.5 Microwave heating of bulk lanthanum polyphosphates

Table 3 shows the maximum diameter of the drilled hole in lanthanum polyphosphate pellets before and after microwave heating. The maximum diameter decreases after microwave heating. Upon microwave irradiation, the bulk samples lost water and became hard yet fragile.

The bulk samples heated by microwave are compared with bulk samples heated in an electric furnace (Table 4). The bulk samples heated in an electric furnace support large drilled holes, with diameters of 6.0 mm and 6.5 mm. The weight loss is less than 5% in these bulk samples. These results are highly desirable; however, the heating time is too long for bulk samples heated in an electric furnace. The rising temperature ratio is 5 K/min in the electric furnace. Therefore, the bulk samples are heated for longer than 3600 s in the electric furnace. Microwave irradiation, which is less than 180 s, is effective in improving the strength against ultrasonication for the bulk samples synthesized by the HHP process.

Table 3 Maximum diameters of drilled holes in lanthanum polyphosphate pellets with and without microwave heating (30 s)

Pressure (MPa)	Water (ml)	Temperature (℃)	Without (mm)	With (mm)
20	0.1	100	4.5	4.5
20	0.1	150	4.5	4.0
10	0.1	100	6.0	4.0
20	0	100	4.5	4.5

Table 4 Heating effects of bulk lanthanum polyphosphates on machinable and vibration strengths (HHP temperature = 100 ℃, pressure = 20 MPa, water volume = 0.1 ml)

Heating	Temperature (℃)	Time (s)	Maximum diameter* (mm)	Weight loss** (%)
—	—	0	4.5	100
Microwave	—	30	4.5	7.24
Microwave	—	60	5.0	4.38
Microwave	—	180	4.5	6.34
Electric furnace	200	3600	6.0	2.36
Electric furnace	300	3600	6.5	1.28

*: machinable strength; **: vibration strength.

3.6 Other rare earth phosphates

According to the XRD analyses, lanthanum orthophosphate, yttrium ortho- and polyphosphates were obtained through heating (Fig. 6). These rare earth phosphates formed the bulk samples through the HHP process. XRD patterns of the samples exhibit no change after HHP, microwave heating, or heating in an electric furnace. In order to study the effects of microwave irradiation, the machinable and vibration strengths of these bulk samples were measured. Some of the bulk yttrium ortho- and polyphosphates broke upon microwave heating. These results could be attributed to lanthanum being a light rare earth element and yttrium being a heavy rare earth element. Therefore, HHP conditions of the yttrium ortho- and polyphosphates are different from those of lanthanum polyphosphate. Table 5 shows the maximum diameter of a drilled hole on bulk rare earth phosphates. Yttrium orthophosphate has a larger diameter with increasing microwave irradiation time. Alternatively, lanthanum orthophosphate exhibits little change in its machinable strength. The difference in the machinable strength decreases with decreasing level of sintering. Table 6 displays the vibration strength of the bulk rare earth phosphates in water. Bulk lanthanum orthophosphate decomposed during ultrasonication for 60 s. The bulk yttrium orthophosphate heated at 200 ℃ in an electric furnace exhibits a large weight loss (48%). Alternatively, the bulk yttrium orthophosphate after microwave irradiation exhibits less weight loss. Microwave irradiation for a short amount of time is an effective method to improve the vibration strength of bulk yttrium orthophosphate. Microwave irradiation may potentially improve the machinable and vibration strengths of bulk rare earth phosphates; however, it is not always a suitable method for all rare earth phosphates.

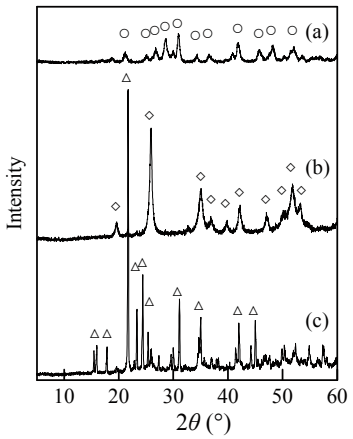


Fig. 6 XRD patterns of samples prepared with (a) La:P = 1:1, (b) Y:P = 1:1, and (c) Y:P = 1:3; ○: $LaPO_4$, ◇: YPO_4, △: $Y(PO_3)_3$.

Table 5 Machinable strength (maximum diameter of hole, mm) of bulk rare earth phosphates

	HHP + microwave heating			HHP + calcination*	
				200 ℃	300 ℃
	30 s	60 s	180 s	3600 s	3600 s
$LaPO_4$	4.5	4.0	4.0	7.0	4.0
YPO_4	5.5	8.5	10.0	7.5	8.5
$Y(PO_3)_3$	—	—	—	7.0	9.5

*: calcination by electric furnace; HHP condition: $LaPO_4$ (100 ℃, 20 MPa, 0.1 ml), YPO_4 (150 ℃, 20 MPa, 0.05 ml), $Y(PO_3)_3$ (100 ℃, 30 MPa, 0.1 ml); —: sample was broken by microwave heating.

Table 6 Vibration strength (weight loss by ultrasound, %) of bulk rare earth phosphates

	HHP + microwave heating			HHP + calcination*	
				200 ℃	300 ℃
	30 s	60 s	180 s	3600 s	3600 s
$LaPO_4$	100	100	100	100	1.40
YPO_4	4.44	3.16	0.86	48.13	0.29
$Y(PO_3)_3$	—	—	—	2.10	0.39

*: calcination by electric furnace; HHP condition: $LaPO_4$ (100 ℃, 20 MPa, 0.1 ml), YPO_4 (150 ℃, 20 MPa, 0.05 ml), $Y(PO_3)_3$ (100 ℃, 30 MPa, 0.1 ml); —: sample was broken by microwave heating.

4 Conclusions

Bulk lanthanum polyphosphate samples were synthesized using HHP process. The resulting bulk samples possessed a filling factor of approximately 70%. A drilled hole greater than 7.0 mm in diameter was obtained on some pellet-shaped bulk samples of 14 mm in diameter. The bulk sample that was not exposed to microwave irradiation crumbled to powders in water, but bulk samples heated by microwave irradiation exhibited little weight loss after ultrasonic treatment. As demonstrated by the bulk sample synthesized through HHP containing a certain degree of water, microwave irradiation for a short amount of time can potentially improve the strength of the material against ultrasonic treatment.

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